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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We have recently extended the gas-phase MPI technique to probe molecules adsorbed on fused quartz surfaces. The phenomenology of the process is rich, showing wavelength-dependent fragmentation patterns. Our first generation surface/mass spectrometer system has a proven detectability limit of $< 4 \times 10^{13}$ molecules of dimethyl methyl phosphonate (DMMP) corresponding to an exposure to a DMMP partial pressure of 1×10^{-7} Torr for 1 second.		

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LASER DETECTION OF CHEMICAL AGENTS

FINAL REPORT

RICHARD N. ZARE

FEBRUARY 1, 1984

U. S. ARMY RESEARCH OFFICE

ARO DAAG 29-80-K-0097
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DEPARTMENT OF CHEMISTRY
LELAND STANFORD JUNIOR UNIVERSITY



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LASER DETECTION OF CHEMICAL AGENTS

We have recently extended the gas-phase MPI technique to probe molecules adsorbed on fused quartz surfaces. The phenomenology of the process is rich, showing wavelength-dependent fragmentation patterns. Our first generation surface/mass spectrometer system has a proven detectability limit of $< 4 \times 10^{13}$ molecules of dimethyl methyl phosphonate (DMMP) corresponding to an exposure to a DMMP partial pressure of 1×10^{-7} Torr for 1 second.

The heart of our experimental apparatus is an 8mm quartz light pipe which passes from outside our vacuum system into the ion source of a quadrupole mass spectrometer (Finnigan Model 3000). Laser light from a Nd-YAG pumped, doubled dye laser (Quanta Ray DCR-i and PDL with Lasermetrics KD*P crystals) was mildly focused into the light pipe, and ionized molecules adsorbed on the light pipe face within the mass spectrometer ion source. These ions were mass analyzed and detected using the Finnigan electronics, the output of which was fed into a boxcar (PARC 162 with 165 plugin) and sent to a strip chart recorder. The chamber was evacuated with a 2" water-baffled diffusion pump and had an attainable base pressure of $< 1 \times 10^{-7}$ Torr.

Dimethyl methyl phosphonate (DMMP) (Aldrich, 97%) was freed from air by several freeze-pump-thaw cycles and was metered into the ionization source through a needle valve and effusive jet.

Figure 1 shows the mass spectrum obtained from the surface at a pressure of 4×10^{-6} Torr and a laser wavelength of 265 nm. The gas-phase ionization under similar conditions is minimal. A comparison with the mass spectrum obtained with electron impact ionization (Figure 2) makes the case against electron-mediated processes quite convincing. The MPI spectrum shows much less, as well as qualitatively different, fragmentation compared to the

electron impact (EI) spectrum. For example, the $m/e=93$ peak in the MPI spectrum results from highly energetic parent ions eliminating methoxy radical, while in the EI spectrum this feature is replaced by the lower energy loss of formaldehyde.

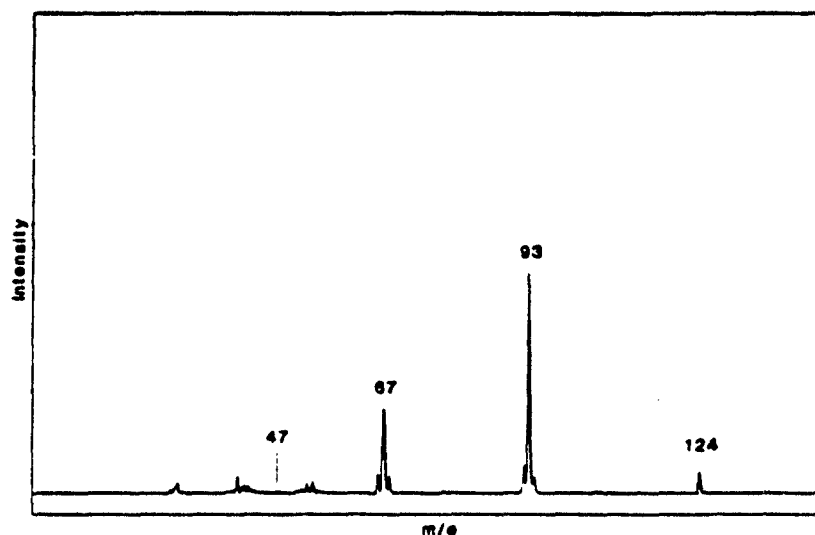


Figure 1. DMMP Mass Spectrum; Surface MPI $\lambda = 265$ nm, $P = 4 \times 10^{-6}$ Torr.

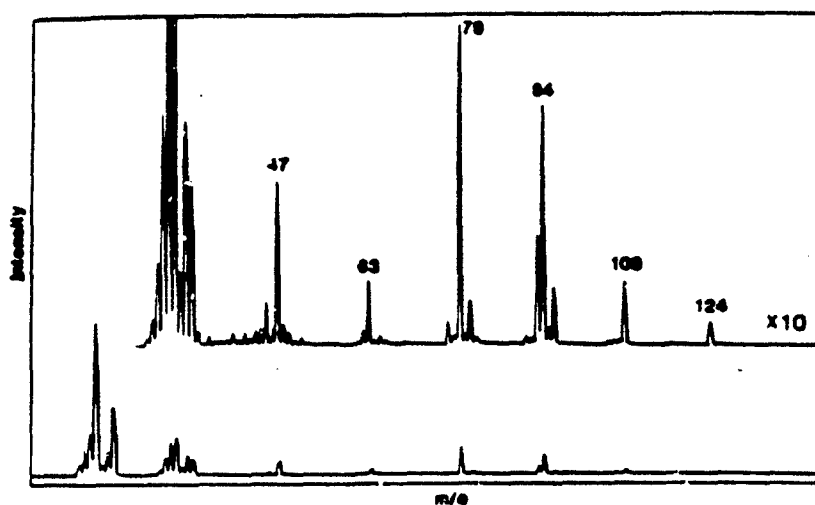


Figure 2. DMMP Mass Spectrum With Electron Impact Ionization; Electron Energy ~ 70 eV, $P = 4 \times 10^{-6}$ Torr.

If the laser wavelength is changed to 290 nm, the mass spectrum obtained is radically different (see Figure 3). There is much more fragmentation, reflecting the fact that the ionization is now a four-photon process, with up to 3 eV of excess energy being deposited in the nascent ion. The $m/e=93$ peak is still in evidence, but the parent ion peak at $m/e=124$ has been replaced by $(M+H)^+$ at $m/e=125$. This probably reflects an ion-molecule reaction occurring in the localized, high density gas cloud at the light pipe surface. The signals at $m/e=125$ and $m/e=93$ are both proportional to the fourth power of the laser intensity, reflecting the multiphoton nature of the process. They are also linear in sample pressure, thus ruling out background (pump oil) contamination as the source of the signal, and allowing us to estimate detection limits for the technique (vide infra).

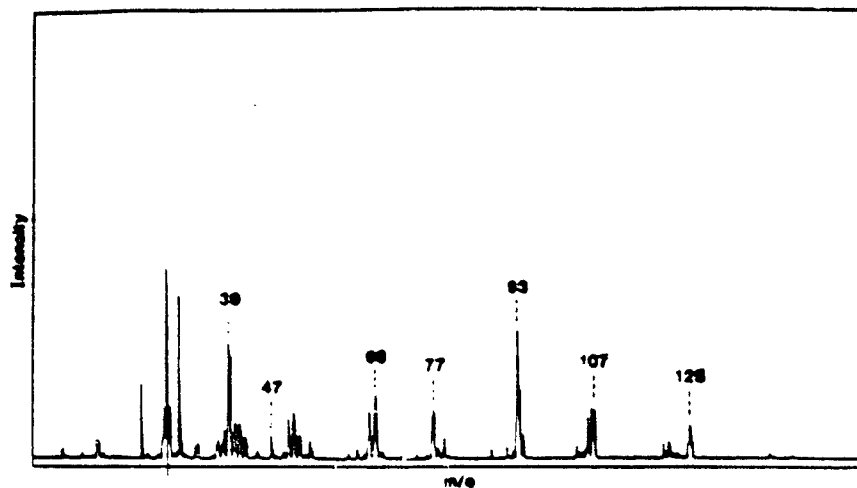


Figure 3. DMMP Mass Spectrum; Surface MPI; λ 290 nm, $P = 4 \times 10^{-6}$ Torr.

LIST OF PAPERS AND MANUSCRIPTS PUBLISHED
DURING THE PERIOD 09/1/80 TO 08/31/83

The appropriate number of copies have already been submitted to the U. S. Army Research Office.

D. Rider, J. Durant, D. Proch, R. N. Zare, "Ion Fragmentation Kinetics by Multiphoton Ionization," Bull. Amer. Phys. Soc. 27, 45 (1982), paper presented at the American Physical Society Meeting in San Francisco, Jan. 25-28, 1982.

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S. L. Anderson, G. D. Kubiak, and R. N. Zare, "Resonance Enhanced Multiphoton Ionization of Molecular Hydrogen via the $E, F^1\Sigma_g^+$ State: Photoelectron Energy and Angular Distributions," Chem. Phys. Lett. (accepted).

Scientific Personnel Supported by This Project:

Ernesto Marinero - Physical Sciences Research Associate
David M. Rider - Postdoctoral Research Associate

No degrees were awarded during this period.